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Low-field orientation dependence of ^{3}He relaxation in spin-exchange cells

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We have observed a significant dependence of ^{3}He longitudinal relaxation times in glass spin-exchange optical pumping (SEOP) cells due only to the physical orientation of the cell in a 3 mT (30 G) applied magnetic field. The cells had no previous exposure to higher fields or were thoroughly degaussed prior to being measured. The presence of rubidium metal and heating of the cells associated with the SEOP process is necessary to produce this low-field orientation dependence. Our data suggest that the magnetic relaxation sites at the glass wall involved here may be the dominant cause of wall relaxation in SEOP cells at any field.

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Hyperpolarized (HP) noble gases (principally ^{3}He and ^{129}Xe) are important for a growing number of applications in physics [1,2], chemistry [3], biology [4], and medicine [5]. The NMR sensitivity of HP gases depends critically on the longitudinal spin-relaxation time T_1. The dominant contribution to T_1 is often due to wall relaxation (characterized by the time T_{1w}), i.e., depolarizing interactions between the gas atoms and the glass container (cell). For production of HP ^{3}He by spin-exchange optical pumping (SEOP) [6], in which ^{3}He nuclei are polarized through collisions with an optically pumped alkali-metal vapor (usually Rb), the presence of alkali metal in heated cells is required. However, even for unheated storage cells in which HP gas is introduced following either spin-exchange or metastability-exchange optical pumping (MEOP) [7], alkali-metal coatings are often used because they are known to yield a significant increase in T_{1w} [8,9] as compared to bare-glass cells [10,11]. The introduction of alkali metal into SEOP cells is also correlated with the appearance of "T_1 hysteresis," a dependence of T_{1w} at a fixed low applied field on previous exposure of the cell to a much larger field [9]. Multidomain magnetic sites at the glass surface were shown to strongly affect wall relaxation at 3.1 mT for cells exposed to magnetic fields between 10 mT and 1 T.

We now report a dependence of T_{1w} on the physical orientation of cells in the low applied magnetic fields ($\approx$3 mT) typically used in SEOP. In contrast with previous work [9], these cells either have had no previous exposure to a large magnetic field ("pristine" cells) or have been thoroughly degaussed, i.e., the cell-wall magnetization has been minimized through exposure to an alternating and gradually decreasing field. We generally observe a significant increase in T_{1w}, due solely to reversing the cell orientation in a 3 mT (30 G) field. This effect has been observed in cells fabricated by two separate research groups (University of Utah and NIST) using several types of glass and a wide range of cell sizes, shapes, and ^{3}He pressures. We expect that the magnetic relaxation sites first observed in Ref. [9] are involved here, as well. However, the heating of cells associated with SEOP also plays a crucial role in producing this low-field orientation dependence. We conclude that the effects of magnetic sites cannot be avoided simply by avoiding large applied fields; indeed, these sites may be the dominant cause of wall relaxation at any field.

Data were acquired on three sets of cells. Sets one and two consist of pristine cells measured for the first time after fabrication (Table I) and degaussed cells (Table II), respectively, with some cells common to both sets. These cells were fabricated and measured at Utah [12]; they are made of blown Corning 7740 (Pyrex) [13] glass with a spherical volume of $\approx$50 cm^3. A 10 cm length of capillary tubing separates the main chamber from a right-angle glass valve, through which the cells are filled to several bar with ^{3}He. Utah cells having the same numerical designation were made at the same time and on the same glass manifold. The third set of cells (Table III) was made of aluminosilicate glass or fused quartz and tested at NIST [1,14,15]. They range in volume from 40 cm^3 to 620 cm^3 and are either permanently sealed SEOP cells or valved MEOP cells. Some were made from completely blown glass, while others were made by optically sealing polished windows onto either blown General Electric (GE) 180 [16] glass cylinders or extruded Corning 1720 [13] glass tubing. Windows were fabricated from GE 180 or ^{10}B-depleted Corning 1720.

TABLE I. Wall relaxation times T_{1w} (in hours) of several pristine Utah Pyrex cells at pressure p. The labels $\mathcal{O}_1$ and $\mathcal{O}_2$ refer to arbitrary but mutually antiparallel orientations in the external 3 mT field, where the ^{3}He is initially polarized in $\mathcal{O}_1$. Measurements are shown chronologically left to right with no intermediate heating and repolarization of the ^{3}He.

Cell	p (bar)	$\mathcal{O}_1$	$\mathcal{O}_2$	$\mathcal{O}_1$	$\mathcal{O}_2$
6B[a]	8.3(0.2)	38.6(1.9)	109(15)		
20A	8.2(0.2)	39.9(1.4)	38.7(1.2)	34.6(2.0)	
20B	8.2(0.2)	52.3(1.9)	50.9(1.6)	44.6(1.0)	
21B	4.8(0.2)	80.8(4.8)	213(10)	69.4(1.8)	
22A	8.2(0.2)	3.3(0.1)	16.8(0.5)	3.8(0.1)	16.2(0.4)
22B	8.2(0.2)	83.3(3.0)	99.9(4.4)	64.0(1.9)	107(3)

[a]This cell is a blown cylinder with rounded ends and a volume of 35 cm^3.

TABLE II. Wall relaxation times T_{1w} (in hours) as measured chronologically from left to right for several degaussed Utah cells at pressure p. For the first eight entries, cells were degaussed again and the ^{3}He was repolarized by SEOP in orientation $\mathcal{O}_2$ prior to the second pair of measurements. For the last three entries, polarized ^{3}He was transferred into the cells (without heating them) prior to the first pair of measurements; they were polarized in the usual way prior to the second pair without intermediate degaussing.

Cell	p (bar)	$\mathcal{O}_1$	$\mathcal{O}_2$	$\mathcal{O}_2$	$\mathcal{O}_1$
5A	8.3(0.2)	59.4(3.9)	97(11)	106(10)	86.6(2.1)
5A	8.3(0.2)	54.7(0.5)	70.2(1.2)	94.0(5.8)	136(5)
9A	8.2(0.2)	22.3(0.9)	60.4(4.1)	18.2(0.3)	46.9(0.6)
15A	8.2(0.2)	18.1(1.8)	21.1(0.6)	18.4(0.4)	20.5(0.3)
20A	8.2(0.2)	36.3(0.4)	36.5(0.4)	34.3(0.5)	33.5(0.4)
20B	8.2(0.2)	43.1(1.0)	52.0(1.4)	36.1(1.1)	48.0(0.9)
22A	8.2(0.2)	13.3(0.5)	51.6(1.4)	17.1(0.8)	38.0(1.0)
22B	8.2(0.2)	73.2(3.0)	74.4(3.7)	78.4(1.6)	95.9(3.5)
6B[a]	2.8(0.2)	39.2(1.4)	41.9(0.4)	40.9(1.2)	48.2(0.5)
22A[a]	3.2(0.2)	27.1(0.1)	25.2(0.2)	14.3(0.1)	30.5(1.0)
22B[a,b]	3.1(0.2)	78.0(2.2)	53.7(1.4)	48.4(1.1)	55.0(0.7)

[a]No heating of these cells prior to first measurement pair.
[b]For the second pair of measurements, this cell was pumped and measured in $\mathcal{O}_1$ and then rotated to $\mathcal{O}_2$.

Unless otherwise noted, all cells contain 10–100 mg of Rb, distilled in during fabrication. ^{3}He was polarized by SEOP for 10–20 h (often overnight) at 170–190 °C. All T_1 measurements were made at room temperature by periodically recording the NMR signal height and fitting the data to a single exponential decay. Utah measurements were made at 3.1 mT using 100 kHz pulse NMR [17]. Between 10 and 20 data points were acquired out to times ranging from 0.7 to 2 times T_1. A typical data set and fit for a Utah cell can be seen in Fig. 5b of Ref. [12]. NIST measurements were made at 2.6 mT using adiabatic-fast-passage NMR [1]. For the NIST data, between 3 and 7 data points were acquired out to times ranging from 0.15 to 0.5 times T_1. A correction was applied for the contribution from bulk ^{3}He-^{3}He collisions to yield T_{1w}. For an 8.0 bar cell at 295 K, the bulk contribution is 101 h [18] and scales inversely with gas density. The uncertainties in T_{1w} (shown in parentheses) result from propagating the statistical relative uncertainty in measured T_1 values ($\leqslant 3\%$ in all cases) through the correction. The relative uncertainty in the bulk contribution itself, due to uncertainty in cell pressure (typically $\leqslant 5\%$) and/or the calculation in Ref. [18], is not accounted for in the tables. It results in a small, purely systematic correction to all T_{1w} values for a given cell.

TABLE III. Properties and relaxation times T_{1w} (in hours) for NIST SEOP cells. The glasses and construction used for the cells are identified using nomenclature discussed in the text. The NIST SEOP cells contain 0.85 bar of ^{3}He, except for the Chekhov cell, which contains 1.25 bar of ^{3}He. "Final range" indicates the range of relaxation times observed for both orientations after, but not including, the initial measurements.

Cell	Wind./cyl.	$\mathcal{O}_1$	$\mathcal{O}_2$	Final range
BamBam	1720/1720	98(2)	155(4)	89–119
Betty	180/1720	295(3)	214(6)	162–515
Mars	180/1720	120(2)	386(7)	187–309
Spock	180/180[a]	37(1)	309(7)	70–165
Chekhov	180[a]	28(1)	222(1)	28–239
Red Baron	180[a]	90(2)	380(49)	

[a]Glass was reblown tubing.

Measurements on the first set of (pristine) cells followed this sequence: the ^{3}He gas was polarized and T_1 measured immediately afterward in a field of 3.1 mT with the cell in some arbitrary but convenient orientation with respect to the external field (denoted by $\mathcal{O}_1$). The cell was then rotated 180° about an axis perpendicular to the applied field to orientation $\mathcal{O}_2$, and another T_1 measurement was made. Up to four T_1 measurements were made for each cell with an intervening orientation change but without heating the cell, repolarizing the gas, or removing the cell from the field. Results of these measurements are shown chronologically from left to right in Table I. All pristine cells showed some form of orientation-dependent behavior; several showed large changes in T_{1w} due simply to reversing the orientation. Three of the six cells (21B, 22A, and 22B) show a pattern of alternating longer and shorter T_{1w} with alternating cell orientation.

The second set of cells had been previously exposed to applied fields >100 mT (1 kG) and were thoroughly degaussed before being measured. The two-step process first employs a 50 rpm motor to rotate a cell about its capillary axis between the poles of an electromagnet while the magnetic field is steadily turned down over about one minute from 1 T to the magnet's remanent field (≈ 3 mT). Next, the cell is held stationary in a decreasing AC magnetic field generated by a tuned 60 Hz series *LC* circuit controlled by a variable AC transformer. The maximum AC field generated by this apparatus is about 140 mT. This method reliably degausses most cells to well below the magnetization induced by an applied field of 10 mT, the order of magnitude observed to correspond to the onset of high-field T_1 hysteresis previously observed in these cells [9,19].

Measurements on degaussed cells followed this sequence: After degaussing, SEOP was performed in a 3 mT field in orientation $\mathcal{O}_1$. A pair of T_1 measurements was then made in $\mathcal{O}_1$ and $\mathcal{O}_2$, similar to the pristine-cell measurements. The cell was then degaussed again and the ^{3}He repolarized at 3 mT in $\mathcal{O}_2$. A second pair of consecutive T_1 measurements was made, with an intervening 180° rotation, starting with $\mathcal{O}_2$. Repolarization of the ^{3}He was necessary after de-Gaussing because the AC degaussing apparatus destroys any existing polarization. Results are shown in Table II. The change in the orientation of initial field exposure and SEOP from $\mathcal{O}_1$ to $\mathcal{O}_2$, with degaussing between measurement pairs, caused the orientation dependence of T_{1w} to be reversed. For two cells (9A and 15A), even the values of T_{1w} were almost

exactly interchanged. We then remeasured three cells (last three rows of Table II) without heating them by using polarized ^{3}He transferred in from another cell for the first measurement pair. Prior to the second measurement pair, these cells were not degaussed but were heated and polarized as before. For two of these three cells, the orientation dependence was absent or minimal for the first measurement pair (where no heating was done) and reappeared in the second pair after heating and SEOP were performed.

For all Utah cells, the ratio of the second measurement in a pair to the first ranged from 0.75 to 5. Only one cell (20A) does not exhibit statistically significant orientation dependence. With the exceptions of the second pair of measurements in the first test of cell 5A and the second pair (after the no-heating test) on cell 22B, all observations of orientation dependence in the Utah cells that are greater than measurement uncertainty exhibit a shorter T_{1w} when measured in the orientation of initial placement in the 3 mT field for SEOP.

The NIST cells were nominally pristine but had been variously heated, polarized, and exposed to low fields prior to the recorded measurements. As part of a now discontinued depolarization procedure, small sections of the cells Betty and Mars may have experienced fields between 10 mT and 50 mT. The NIST cells were never degaussed. Results are shown in Table III, where ''Final range'' refers to the range of T_{1w}'s observed for both orientations in a few subsequent cycles of SEOP. Observations of orientation dependence in the NIST cells, both for the measurement pairs listed in Table III and for the seven additional pairs in the data summarized in ''Final range,'' exhibited a shorter T_{1w} when measured in the orientation of initial placement in the 3 mT field for SEOP. The only exception to this rule is the first pair on the cell Betty. However, the average magnitude of the orientation dependence decreased for some cells, such that the ratio of the second measurement in the pair to the first only exceeded a factor of 2 in three of these seven cases. Six additional measurements with the cells Spock and Chekhov were obtained with the magnetic field turned off for the heating and/or cooling cycle, and in these tests the sign of the orientation dependence was less consistent. Further investigation is required to understand the role of the field during temperature cycling.

We then used the MEOP method and a polarized gas compression apparatus [15] to fill three valved, blown cells: Europa and Antares (blown 180 glass, filled to 0.85 and 0.5 bar, respectively) and Spica (blown fused quartz, filled to 0.5 bar). The Europa cell contained no Rb, and the Antares cell had never been heated after distillation of Rb. For the Spica cell, data were acquired before and after heating to 180 °C. The relaxation times of these cells were tested at four or six field magnitudes between $+2.6$ mT and -2.6 mT without physical reversal of the orientation of the cell. For Europa and Antares, the range of relaxation times obtained was 29 h–32 h and 119 h–124 h, respectively, which indicates essentially no orientation dependence within uncertainties. For Spica, the range of relaxation times obtained before heating was 230 h–253 h, while the range after heating was 119 h–258 h. Hence Spica showed very little orientation dependence before heating, but it was clearly apparent after heating.

The orientation dependence of T_{1w}, consistently observed in all data sets, indicates that cell-wall magnetization induced by applied fields as low as 3 mT is detectable in the measured ^{3}He relaxation times in almost all SEOP cells. We note that effects due to magnetic field gradients [20] were very small and in any case cannot be responsible for orientation dependence, because the cells were always rotated about their centers and always occupied the same volume at the center of the Helmholtz pair. Cells were generally pumped into the low-energy Zeeman state to avoid losses from stimulated emission (masing) [21]. Some of the Utah cells were pumped into the high-energy Zeeman state; no unusual behavior in the spin-relaxation data that would indicate masing was observed. As of yet, no correlation has been observed between the presence or degree of orientation dependence and the Zeeman state.

The data further indicate that both the presence of Rb and heating after distillation are required to produce low-field orientation dependence. Most cells (including all those exhibiting orientation dependence) were heated for SEOP and had their initial T_1 immediately measured in the same orientation. The subsequent 180° rotation to $\mathcal{O}_2$ (done at room temperature) apparently leads to a decreased cell-wall magnetization, resulting in a longer T_{1w}. In contrast, unheated cells into which polarized gas was transferred exhibited little or no orientation dependence, whether they had never been heated after Rb distillation (NIST cells) or had not been heated since last being degaussed (Utah cells). However, the data in Table I (where orientation was reversed up to three times in succession) indicate that once orientation dependence is present, changes in T_{1w} can occur due to magnetic history, even in the absence of further heating. The return to $\mathcal{O}_1$ typically results in a shorter T_{1w}, indicating that the original orientation dependence is preserved in sign, if not always in magnitude.

For cells that have only been exposed to low fields, it is not clear from the data whether degaussing at room temperature has any effect on T_{1w}. Orientation dependence in the NIST cells seems to be correlated exclusively with the orientation in which the cell is heated for SEOP. However, degaussing did appear to remove any residual orientation dependence for two of the three cells employed in the no-heating experiment (6B and 22A, but not 22B).

We speculate that the wall relaxation rate is proportional to the cell-wall magnetization, which can be ''set'' in a specific orientation by the temperature cycling in low field associated with SEOP. The origin of this magnetization is unknown; possibilities include the Rb in combination with impurities originating in either the glass or the Rb itself, or perhaps the Rb alone [22,23]. Our recent observation of T_1 hysteresis in quartz cells [24], which have substantially less iron than Pyrex, suggests that impurities in the glass may not be the dominant issue. Further study is underway to sort out the effects of field cycling, temperature cycling, degaussing, field reversal versus orientation reversal, as well as to investigate possible physical mechanisms for the observed effects.

There are several cases where the longer T_{1w} of themeasurement pair is a substantial fraction of the bulk limit. These results suggest that eliminating the magnetic sites that cause orientation dependence will further the goal of producing bulk limited cells. Further studies are needed to determine if cells with relaxation times near the bulk limit also show minimal orientation dependence and T_1 hysteresis.

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